CORROSION PROTECTION OF ALUMINUM ALLOYS BY VANADATE PIGMENTS IN EPOXY PRIMERS

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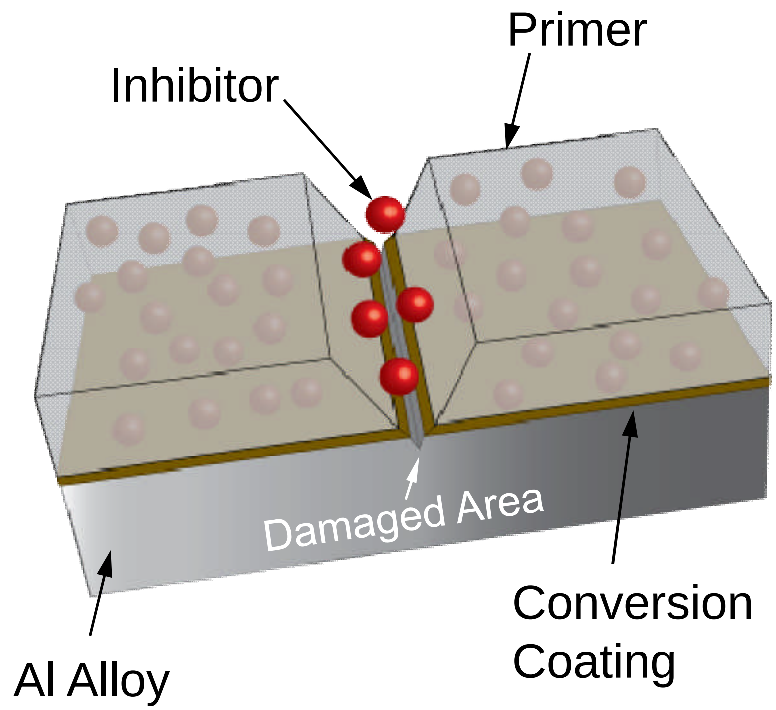
Traditional Protection Schemes for Al Alloys

- Aluminum alloys for the most demanding aerospace applications are protected by Chromate based systems → have to be replaced due to Cr^{6+} toxicity.
- Coating systems based on the release of anionic (or cationic) species
- **These species have to be corrosion inhibitors**



Release of an anionic/cationic specie from the coating to the damaged area.

Objective: To Evaluate the performance of metavanadates as pigments for epoxy-based coatings

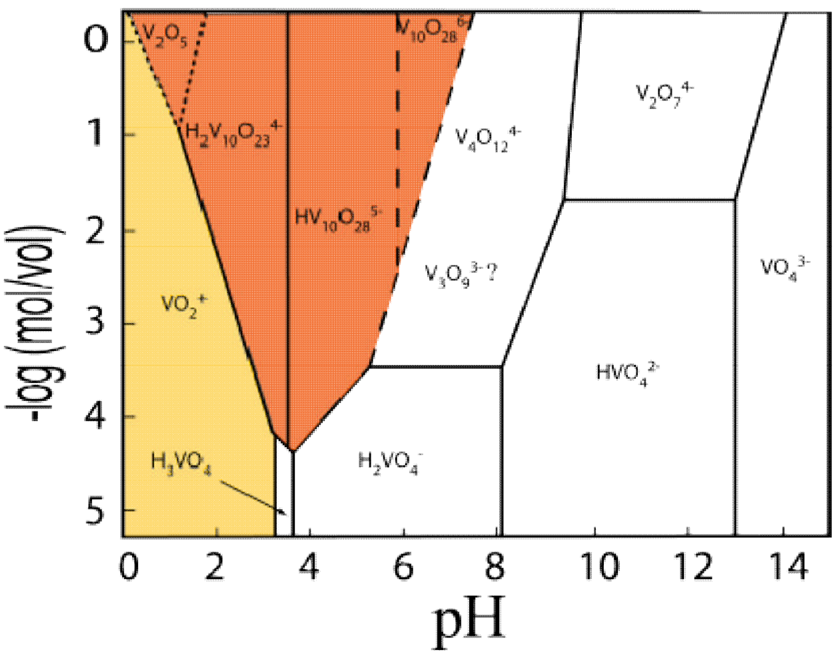
Overview

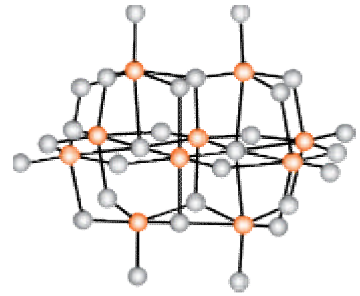
Introduction

Inhibition Mechanisms – Aqueous Solutions

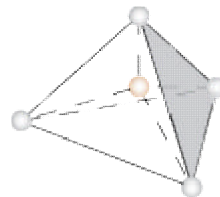
Metavanadates as Pigments in Organic Coatings

Vanadate Speciation – A complex System





Decavanadate $[V_{10}O_{28}^{6-}]$ ion made up of 10 VO_6 octahedra



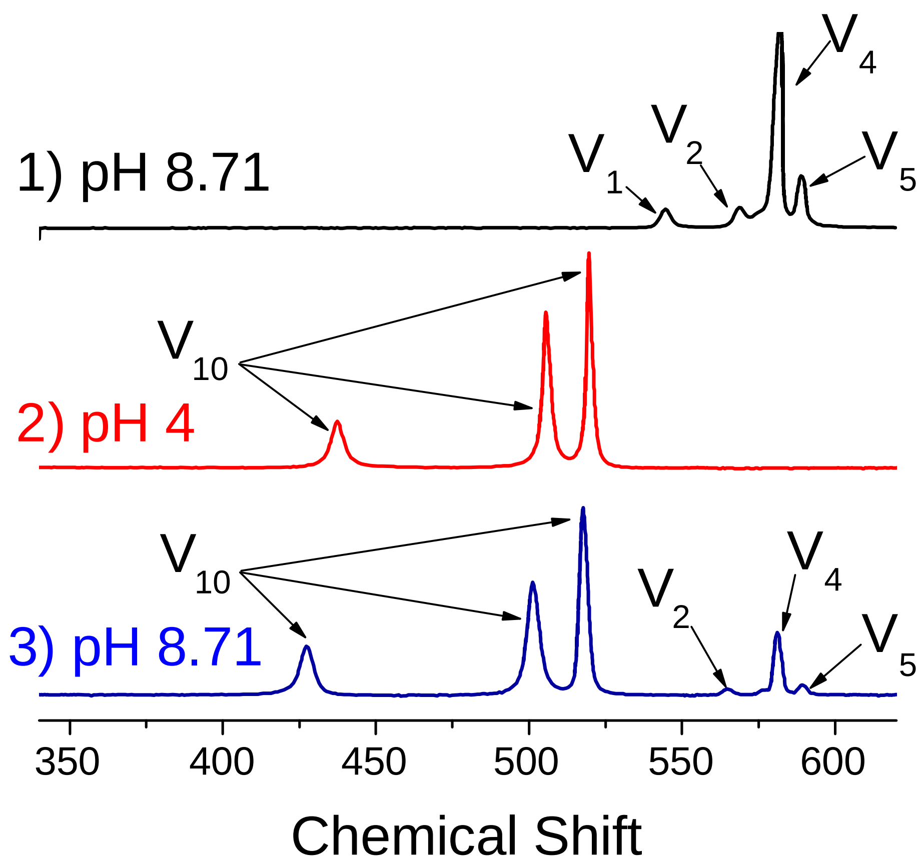
All monovanadates are tetrahedrally coordinated

- Metavanadates = V_1, V_2, V_4 and V_5
- Decavanadates = V_{10}
- **Metavanadate** solutions remain colorless.
- Solutions containing **decavanadates** become yellow-orange.

M. Iannuzzi, PhD Dissertation, The Ohio State University (2006)

Effects of Environment - pH

1. Initial solution - 100 mM $NaVO_3$
2. Acidified to pH 4 by addition of HCl
3. Readjusted to pH 8.71 with NaOH



- Acidification to pH 4 polymerizes all the metavanadates to form V_{10}
- Re-adjusting pH to 8.71 partially de-polymerizes V_{10} to form V_2, V_4 and V_5 but no V_1
- V_4 is the predominant metavanadate specie at pH 8.71
- **All colored solutions contain V_{10}**
- **No colored solutions contain V_1**

MONOVANADATES – Alkaline

DECAVANADATES - Acidification

M. Iannuzzi, PhD Dissertation, The Ohio State University (2006)

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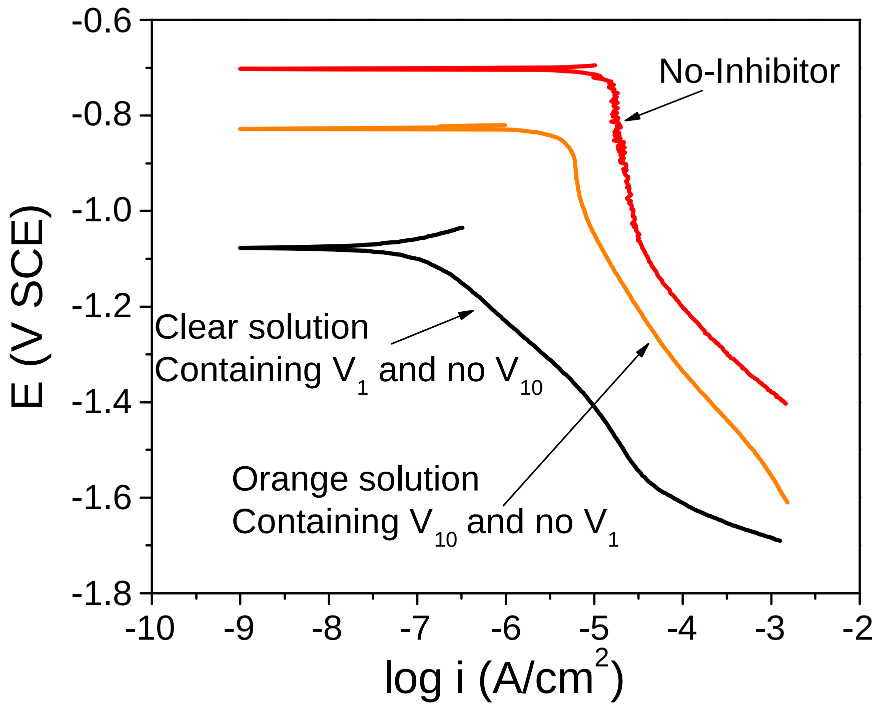
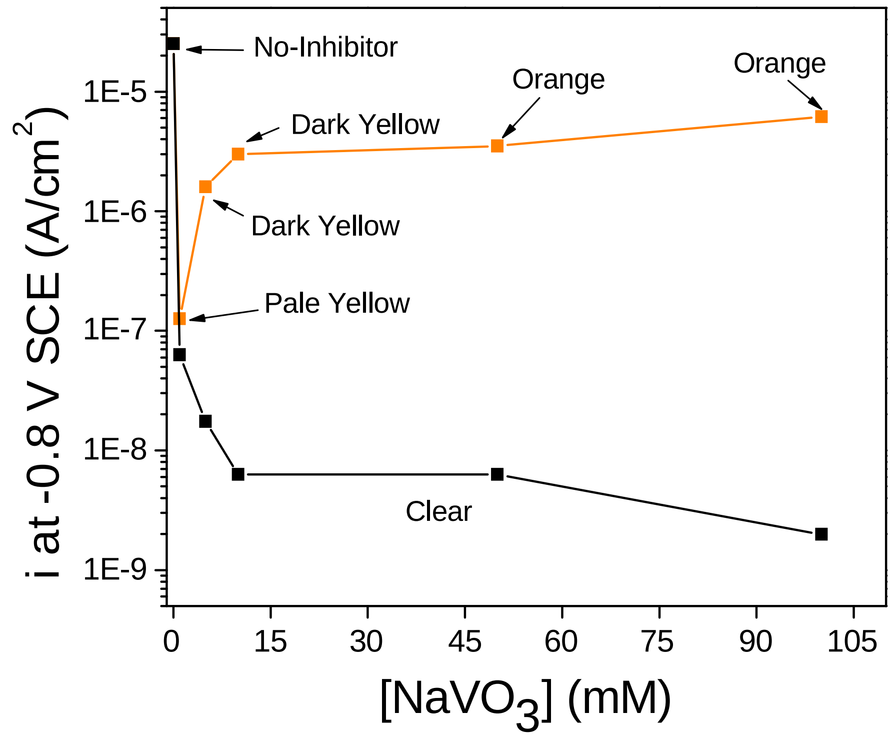
Inhibition Mechanisms

AA2024-T3 in aerated 0.5 M NaCl





- Presence of monovanadate (V_1) is critical for obtaining the largest decrease in O_2 reduction kinetics
- Inhibition increases with incremental [V_1]
- Inhibition decreases with incremental [V_{10}]

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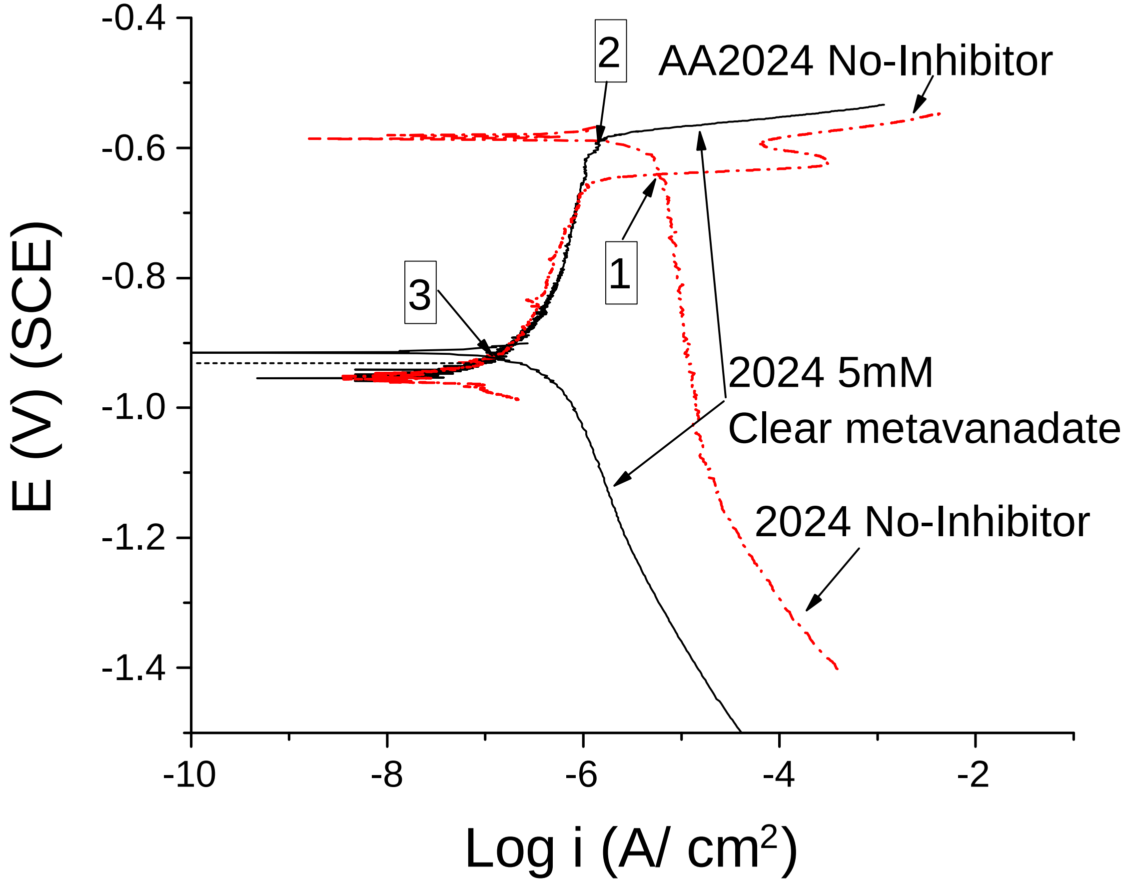
Inhibition Mechanisms (Cont.)



- Monovanadates had a large effect on AA2024 cathodic curve.
- Monovanadates increased the pitting corrosion potential (E_P) of S-Phase particles
- Intersection in passive region.

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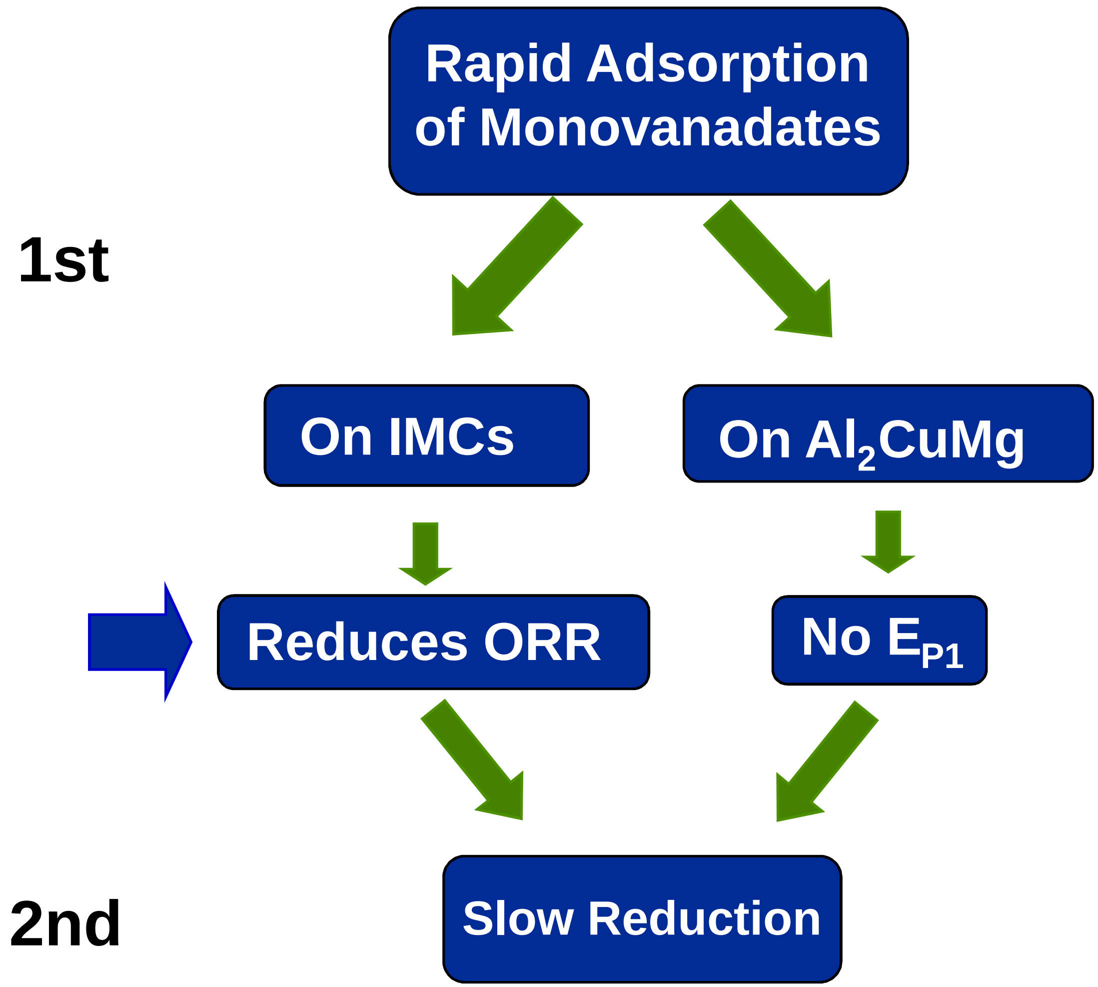
Inhibition Mechanisms - Summary



Overview

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Inhibition Mechanisms – Aqueous Solutions

Metavanadates as Pigments in Organic Coatings

Vanadates as Pigments in Organic Coatings

- The extraordinary inhibition efficiency of **clear metavanadate** solutions suggested that monovanadates could be used in coating formulations as corrosion inhibitor.
- Guan and Buchheit developed a **conversion coating** based on **acidic** vanadate formulas. However, those coatings did not impart the same extent of protection as CCC.
- Multilayer protection schemes rely on the release of the inhibitor to a damaged area. Release can be controlled by a concentration gradient or it can be smartly manipulated.
- Smith et al. and Nazarov et al. used several vanadate pigments such as strontium metavanadate and magnesium metavanadate with good results →**speciation?**
- **Can we find a vanadate pigment that will release monovanadate to a damage area?**

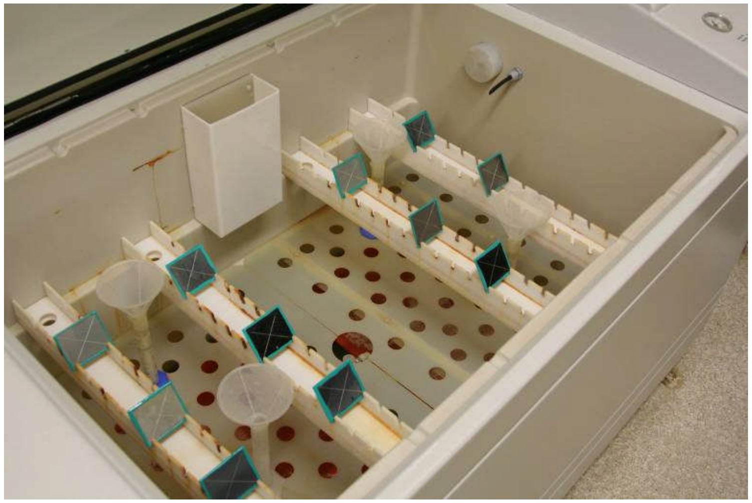
Procedure

- An inhibitor-free aeronautical epoxy-base primer from Henkel was used.
- $NaVO_3$ powder was added to the primer (2 wt%) and sonicated for 1h.
- Curing agent added prior application.
- Coatings sprayed on pre-cleaned AA2024-T3 panels.
- After curing a set of samples was scribed and exposed to the salt fog chamber for 2 weeks (two 1-week exposures). Duplicates.
- Samples were analyzed by EIS, SEM-EDS, and optical microscopy

Plain Epoxy - Control

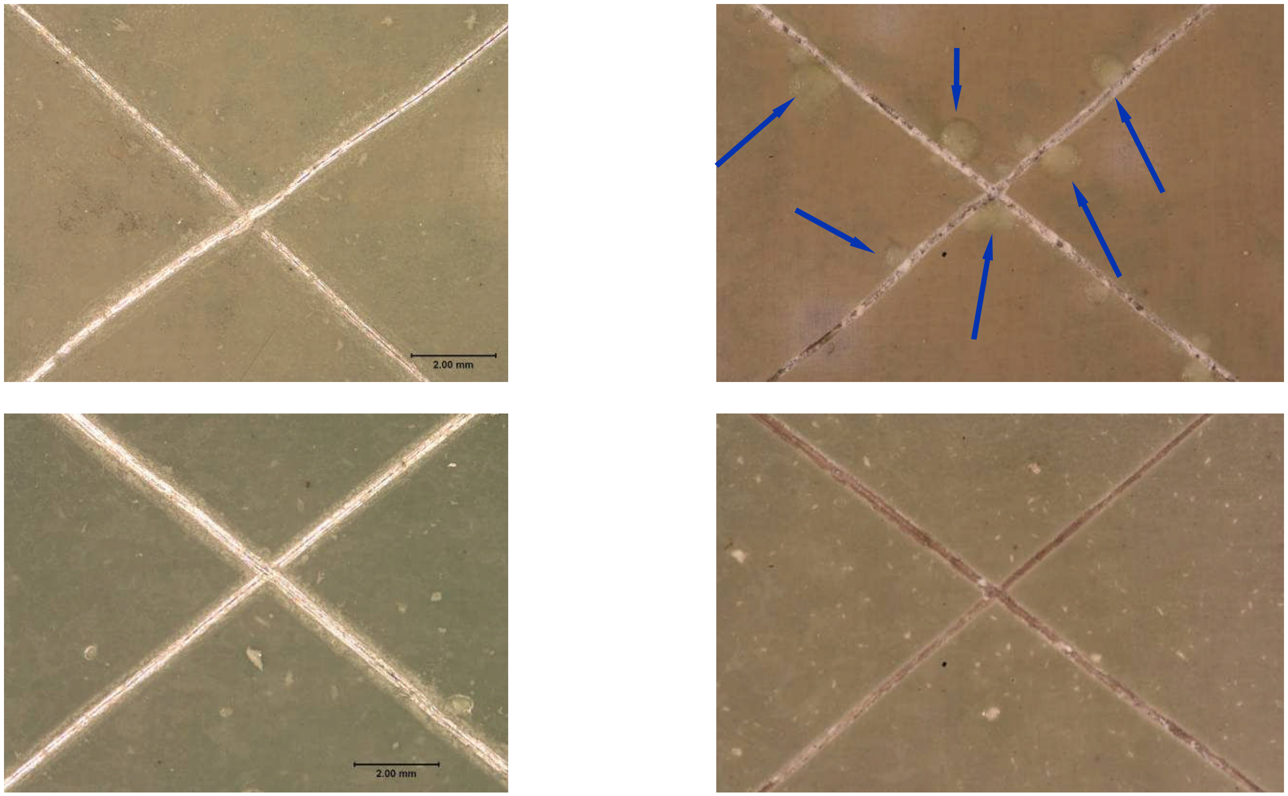
Epoxy + Cr^{+6} - Control

Epoxy + $NaVO_3$



ASTM B117 Test Setup

Salt Fog after 2 Weeks

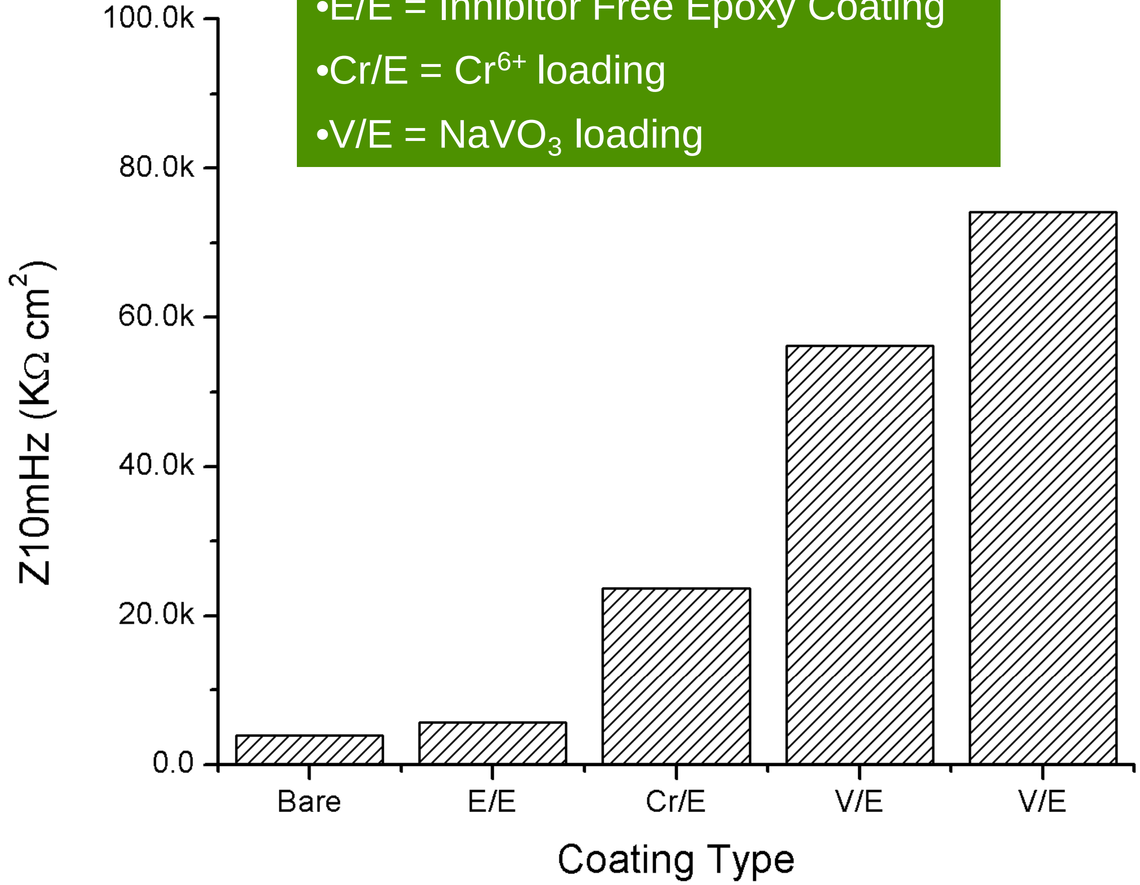


BEFORE AFTER

- Blistering on the plain epoxy control specimens occurred after 1 week.
- No corrosion products or blistering observed on the specimens coated with epoxy+$NaVO_3$ even after 2 weeks of exposure.

EIS after 2 Weeks Exposure

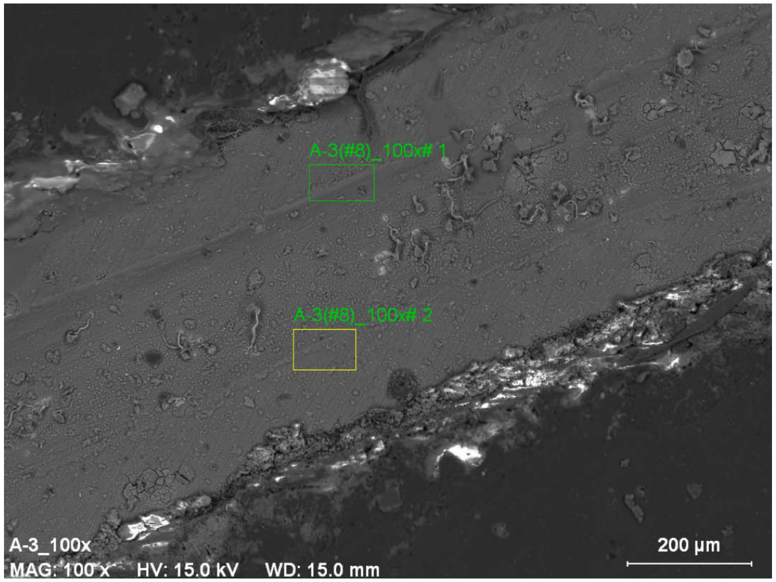
- Bare = As-polished AA2024 sample
- E/E = Inhibitor Free Epoxy Coating
- Cr/E = Cr^{6+} loading
- V/E = $NaVO_3$ loading

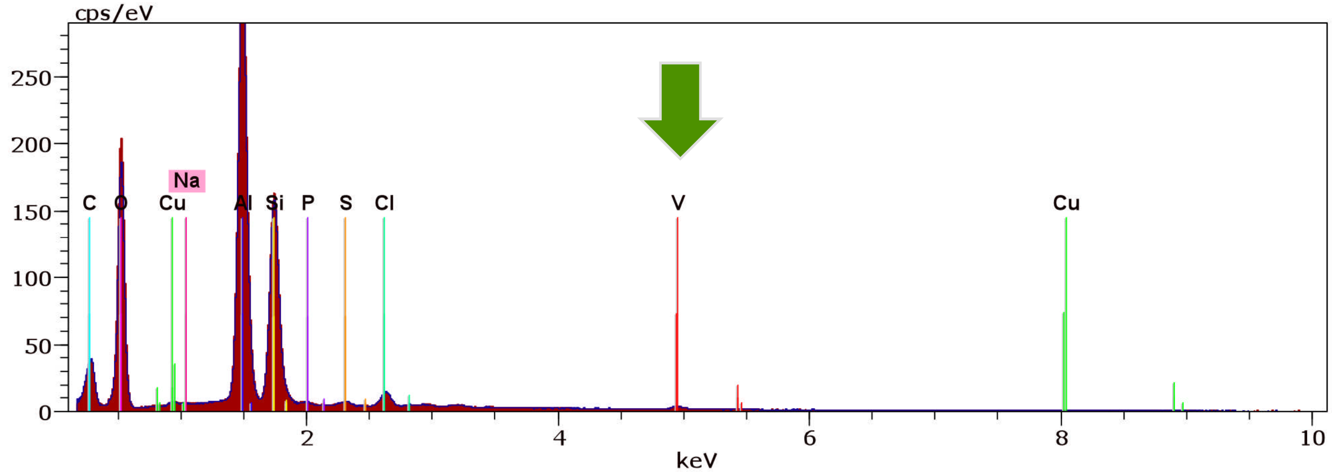


- Samples loaded with $NaVO_3$ showed a significantly larger low frequency impedance value, inline with the absence of attack shown previously.

SEM-EDS Analysis

- The improved corrosion protection imparted by coatings loaded with $NaVO_3$ likely related to the diffusion of metavanadates from the coating to the scribe.
- SEM-EDS was used to evaluate whether traces of vanadium could be detected at the bare Al surface.





Traces of vanadium found along the scribe

Ongoing Work

- Artificial scratch cell:
  - The artificial scratch cell setup is being used to further evaluate whether metavanadates released from the coating could protect bare Al surfaces.

- Coating degradation:
  - A detailed EIS analysis on coatings with and without intentional defects is also being conducted. Results thus far have shown lower **break point frequencies** and larger $\mathbf{Z_{10mHz}}$ values when vanadates were added to the primer in line with the results of ASTM B117 testing.

- Inhibition studies on aeronautical magnesium alloys by metavanadates are being conducted.

Conclusions

- Adding **$NaVO_3$** to plain epoxy primers **greatly improved coating performance**.
- In the presence of metavanadates **no blistering** or corrosion products were found after 2 weeks of exposure to the salt fog chamber.
- Vanadium was found along the scribe, likely suggesting diffusion of the inhibitor from the coating to the bare Al surface.
- The slightly alkaline environment of the chamber could reduce the risk of decavanadate precipitation.

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